UTIC ERE COPY

OFFICE OF NAVAL RESEARCH

Technical Report No. 101

An in situ Surface Fourier Transform Infrared Study of the Adsorption of
Isoquinoline at a Stationary Mercury Electrode

by

D.J. Blackwood and S. Pons

Department of Chemistry
University of Utah
Salt Lake City, UT 84112

DTIC
ELECTE
S NOV 1 4 1988
D
H

July 15, 1988

88 11 10 061

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE		Approved for public release and sale. Distribution unlimited.	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) ONR Technical Report No. 101		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION University of Utah	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry Henry Eyring Building Salt Lake City, UT 84112		7b. ADDRESS (City, State, and ZIP Code)	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-83-K-0470-P00003	

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
Chemistry Program, Code 1113 800 N. Quincy Street Arlington, VA 22217	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)
An in situ Surface Fourier Transform Infrared Study of the Adsorption of Isoquinoline at a Stationary Mercury Electrode

12. PERSONAL AUTHOR(S)
D. Blackwood and S. Pons

13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 9/87 TO 7/88	14. DATE OF REPORT (Year, Month, Day) July 15, 1988	15. PAGE COUNT 24

16. SUPPLEMENTARY NOTATION

17	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	infrared spectroelectrochemistry ,adsorption, mercury

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Attached.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Stanley Pons	22b. TELEPHONE (Include Area Code) (801)581-4760	22c. OFFICE SYMBOL

ABSTRACT

Subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) was used to follow the potential dependent reorientations undergone by isoquinoline molecules that are adsorbed at a mercury electrode surface. The differences in the relative intensity changes on reorientation between the in-plane and out-of-plane vibrational modes have been explained in terms of field-induced infrared absorption.

AN IN-SITU SURFACE FOURIER TRANSFORM INFRARED STUDY OF THE ADSORPTION OF ISOQUINOLINE AT A STATIONARY MERCURY ELECTRODE

DANIEL J. BLACKWOOD and STANLEY PONS *

Department of Chemistry, University of Utah, Salt Lake City, UT 84112 (U.S.A.)

(Received 6th October 1987; in revised form 25th January 1988)

ABSTRACT

Subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) was used to follow the potential dependent reorientations undergone by isoquinoline molecules that are adsorbed at a mercury electrode surface. The differences in the relative intensity changes on reorientation between the in-plane and out-of-plane vibrational modes have been explained in terms of field-induced infrared absorption.

INTRODUCTION

The adsorption of isoquinoline on mercury surfaces has been previously studied by electrocapillary methods [1], ellipsometry [2], double layer capacity measurements [3], and a range of potential step techniques [4–7]. The interest in this system is due in part to the fact that one observes well defined transitions in its physical properties as the molecules undergo transitions in surface orientation and packing under certain experimental conditions.

Isoquinoline molecules can be adsorbed on mercury in four different orientations (Fig. 1). The previous investigations indicate the following behavior for the isoquinoline orientation as a function of potential and concentration: at low negative potentials and low bulk concentrations, the molecules are believed to lie flat on the mercury's surface (molecular plane parallel to the surface). However, on increasing either the potential (in the negative direction) or the bulk concentration, the isoquinoline molecules are forced up into either the 4,5 position [2] or the 5,6 position [1]. This reorientation occurs gradually with the changing coordinates, and

---

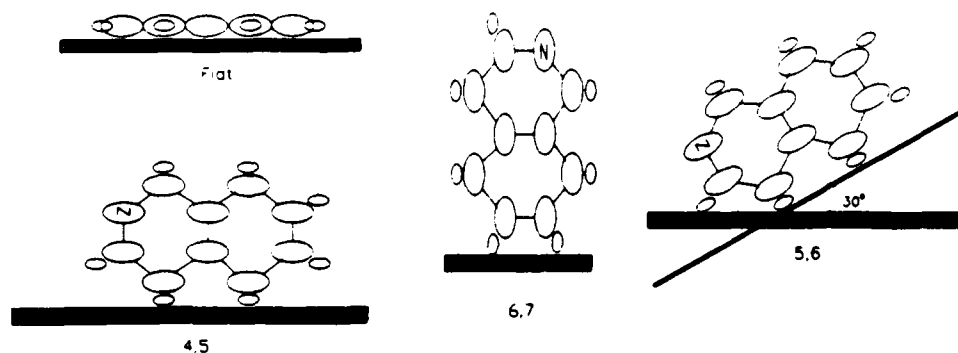* To whom correspondence should be addressed.

Fig. 1. Possible orientations for the adsorption of isoquinoline on mercury.

proceeds through a series of phases containing mixtures of these three orientations of isoquinoline molecules.

Increases in the potential to more negative values, and at sufficiently high concentrations, results in an abrupt reorientation to the 6,7 position. The reason that this second transition is much sharper than the first lies in the fact that mixed phases which would contain the 6,7 orientation are energetically less favorable than
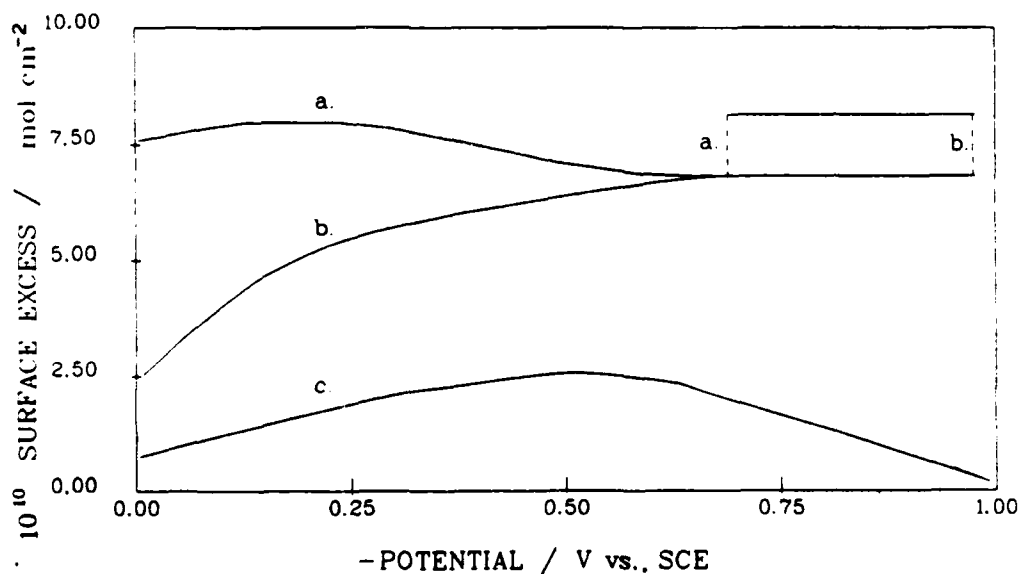

Fig. 2. Superficial excess as a function of potential for a mercury electrode in contact with 0.5 mol dm^{-3} Na$_2$SO$_4$ and the following isoquinoline concentrations: (a) 2.1×10^{-2} (saturated), (b) 6.3×10^{-3}, and (c) 2.1×10^{-4} mol dm^{-3}. (Data from Gierst and co-workers [1])

a complete monolayer of any of the pure standing orientational phases. Gierst and co-workers [1] have produced a graph showing the dependence of the superficial excess on both potential and bulk concentration from their electrocapillary data; we reproduce some of their data in Fig. 2.

This well defined system offers an excellent opportunity for surface infrared reflectance spectroscopic investigation. The infrared study of mercury electrode surfaces has been impeded by experimental difficulties in cell design and optical considerations; the methods used herein are adapted from a configuration that has been used by Bewick and co-workers [8] for some time.

For an isoquinoline molecule adsorbed onto the surface of mercury, the component of its total dipole moment that is perpendicular to the surface will increase as its orientation changes from:

Flat–4,5–5,6–6,7

It is well established (from considerations of the surface selection rules for infrared radiation reflection from metal surfaces and its interactions with adsorbed species) that infrared radiation will be absorbed most strongly by vibrational modes that have a component of the dipole derivative (with respect to the normal coordinate) normal to the metal surface. One thus predicts that as the isoquinoline molecule reorients in the order listed above, the absorption of infrared radiation by the in-plane vibrational modes should generally increase, while the out-of-plane modes should generally decrease. In the flat orientation there is no component of the dipole moment perpendicular to the surface for the in-plane modes. However, infrared active modes (and in some cases infrared forbidden transitions) can still be observed due to field-induced infrared adsorption [9–12].

[9–13]

EXPERIMENTAL

Isoquinoline (Aldrich 97%) was purified further by refluxing with BaO for 30 min and distilling under vacuum. The resulting white crystalline solid had a melting point of 26°C. The purified isoquinoline was stored in the dark, at 0°C and under an argon atmosphere. Mercury was triple distilled (American Scientific) and all other chemicals were of AnalaR grade quality. All solutions were prepared with triply distilled water. All glassware was cleaned in 50 + 50 (v/v) mixture of HNO_3 and H_2SO_4, rinsed with triply distilled water and steamed (triply distilled water) for half an hour. A thin layer cell was designed (Fig. 3) which could be mounted in a vertical position on the spectrometer. The mercury was held in position by a simple glass tube, and electrical contact was achieved with a piece of platinum wire, dipped directly into the mercury. All potentials reported are with reference to a saturated calomel electrode.

The FTIR spectrometer used was a vacuum bench Brucker IBM Model IR/98, modified so that the optical beam was brought upwards through the sample compartment and made to reflect from the bottom of the horizontal mercury
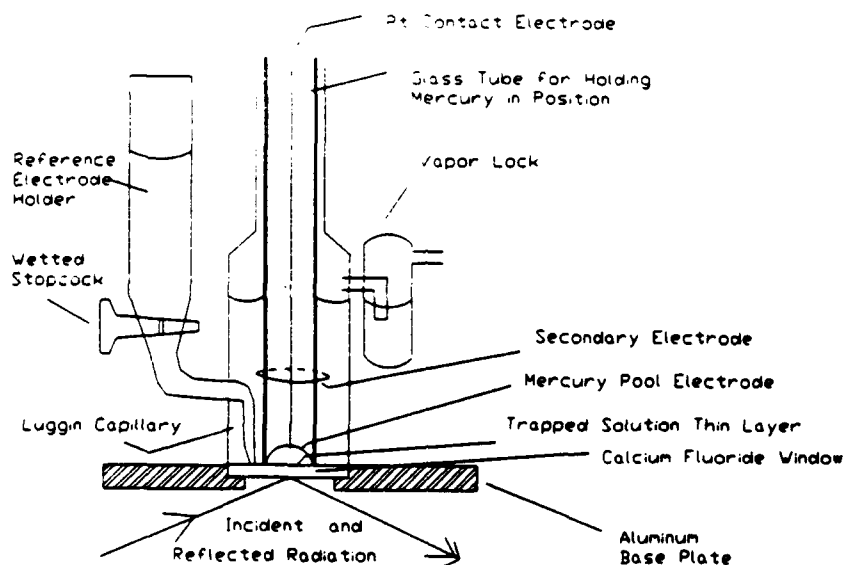
4

Fig. 3. Construction of the thin layer mercury reflectance cell used for all experiments.

surface. The design for the system for performing infrared reflectance experiments from mercury has been described by Bewick [8].

RESULTS AND DISCUSSION

The abrupt transition to the 6,7 orientation manifests itself in cyclic voltammetry as a sharp current spike (Fig. 4). The cathodic spike was found to contain a charge of 2.9 μC cm^{-2}, while its anodic counterpart contained 3.3 μC cm^{-2}. The peak separation was 100 mV, although this relatively large value is due in part to the high iR drop present in thin layer cells.

Figure 5 shows typical SNIFTIRS spectra for isoquinoline molecules adsorbed on mercury. The reference spectrum in each case was obtained at 0.0 V vs. SCE reference electrode; at this potential the molecules are believed to be oriented flat on the metal surface. The vibrational frequencies of the band structure (positive values of absorbance) are easily assigned since they are essentially the same as those reported by Wait and McNerney [14] for pure isoquinoline. The differences in the spectra are that the bands for the adsorbed species exhibit blue shifting of 3–4 cm^{-1} relative to the neat material, and the relative intensities of the bands in each case are markedly changed.

The major vibrational modes observed for isoquinoline are listed in Table 1. The assignments made by Wait and McNerney [14] are also included. The authors made their assignments from considerations of the higher $D_{\infty h}$ symmetry parent species, instead of the C_s symmetry group; they demonstrated that the assignments arising from this representation are reasonable.
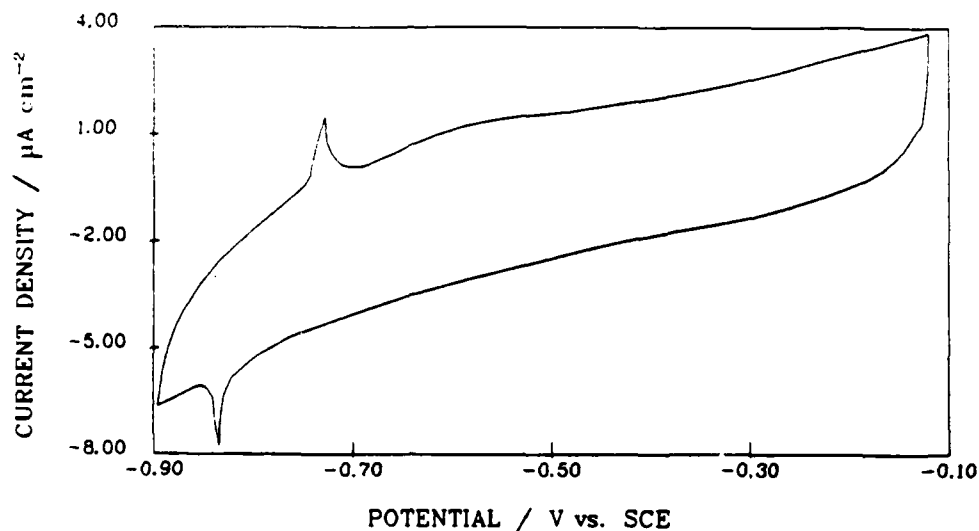
Fig. 4. Cyclic voltammogram for a mercury electrode in contact with a solution 2.1×10^{-2} mol dm^{-3} in isoquinoline + 0.5 mol dm^{-3} Na$_2$SO$_4$ at 10 mV s^{-1}.

The absence of band with negative absorbances in these difference spectra is probably due to the fact that the vibrational frequencies of the bands do not exhibit potential dependence (Fig. 5), and that this species is adsorbed over the entire
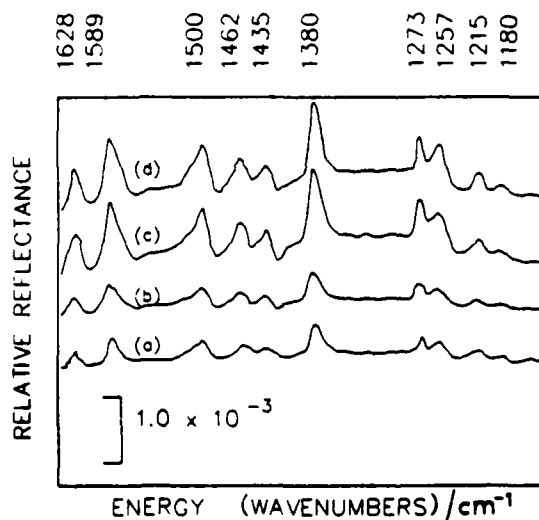

Fig. 5. SNIFTIRS difference spectra for a mercury electrode in contact with a solution that is 1.3×10^{-2} mol dm^{-3} in isoquinoline. Reference potential at 0.0 V vs. SCE, sample potential (a) -0.60, (b) -0.75, (c) -0.80 and (d) -0.9 V vs. SCE.

6

TABLE 1

Assignments of the major infrared bands for isoquinoline at the mercury water interface

Band	Assignment	C_s	D_{2h}	In- or out-of-plane
1628	ν_8	A'	B_{3g}	In
1589	ν_9	A'	A_g	In
1575	$\nu_{26} + \nu_{38}$	$A' + A''$	$A_g + B_{3u}$	In + Out
1500	ν_{11}	A'	B_{2u}	In
1462	ν_{12}	A'	A_g	In
1435	ν_{13}	A'	B_{3g}	In
1380	ν_{14}	A'	A_g	In
1376	ν_{15}	A'	B_{1u}	In
1273	ν_{17}	A'	B_{1u}	In
1257	ν_{18}	A'	B_{2u}	In
1215	$\nu_{36} + \nu_{42}$	$A'' + A''$	$A_u + B_{1g}$	Out + Out
1180	ν_{19}	A'	B_{3g}	In

potential region investigated. This is consistent with results of electrochemical double layer experiments. The spectra then represent relatively simple changes in the absorption of infrared radiation. The intensities of the bands are markedly potential dependent; an especially large change in the intensities is observed at potentials where the orientation changes to the vertical 6,7 configuration.

A unique characteristic of infrared spectra for species adsorbed on electrodes is the potential dependence of the frequency of certain vibrational modes. Two types of mechanisms have been proposed to explain the potential dependent shift of vibrational frequencies. The first involves molecular orbital arguments; the second is based on arguments for interactions between the electric field across the double layer and the highly polarizable electrons of the adsorbed molecule (an electrochemical Stark effect). In the molecular orbital mechanism, electrons can be donated to empty metal orbitals through σ-type overlap with filled ligand orbitals of the appropriate symmetry. The metal can "back" donate electrons from filled d-orbitals to empty π^* antibonding orbitals on the adsorbate. When a molecule is adsorbed on a clean uncharged metal surface, its vibrational frequency may either increase or decrease from the frequency of the unadsorbed molecule depending upon the relative contributions of the σ- and π-bonding interactions. If the π-bonding interaction is dominant the frequency will decrease; conversely, the frequency will increase if the σ-bonding interaction is dominant. When the charge on the electrode is made negative, the bond is weakened due to donation of charge from the metal into adsorbate π^* orbitals and the band frequency shifts to lower wavenumber. When the charge on the metal is made positive shift to higher frequency occurs. At a mercury electrode, however, there are no p- or d-electrons available to participate in a back-bonding interaction. The observation of potential dependent frequency shifts is therefore not expected according to this model.

The electric field mechanism involves coupling of the electric field across the double layer with highly polarizable electrons of the adsorbate. According to the
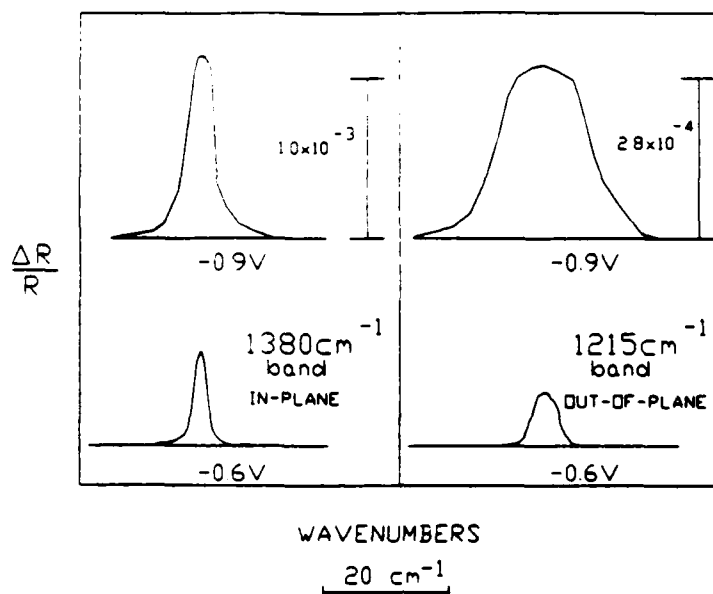
WAVENUMBERS

20 cm⁻¹

Fig. 6. Expanded section of Fig. 5 showing examples of differences in the magnitude of integrated area for two absorption bands with the same changes in electrode potential. The potentials for the difference spectra are -0.6 and $+0.9$ V. The change in area for the 1380 cm^{-1} in-plane mode has increased by a factor of ≈ 4, whereas that of the 1215 cm^{-1} out-of-plane mode has increased by a factor of ≈ 10.

Gouy–Chapman–Stern model, for high concentrations of supporting electrolytes, most of the potential drop will occur within the first 0.5 to 1 nm of the electrode surface, and the drop will be approximately linear with distance. When a layer of adsorbed species is present, it can act as a dielectric across which the greatest portion of the potential drop will occur. Electric fields of the order of 10^9 V m^{-1} can exist in this region. Interaction of this electric field with the dipole moment of the molecule leads to changes in the vibrational frequency of the molecule.

The absorbances in Fig. 5 have positive values. This indicates that the absorption of infrared radiation is strongest when the isoquinoline molecules are lying flat on the electrode surface (in these difference spectra, positive values of absorbance denote stronger absorption at the positive potential, i.e. potentials where the isoquinoline is adsorbed in the flat configuration). This is an opposite result from that suggested from the surface selection rule, and suggests that there is a strong field-induced absorption for the in-plane modes in this configuration, similar to that observed in previous work for pyrene adsorbed on platinum (11).

There are marked differences in the changes in intensity of the in-plane and out-of-plane modes of the adsorbed isoquinoline with potential (Fig. 6). The normalized intensities (against their intensity at -0.1 V vs. SCE) of the vibrational bands shown in Fig. 5 were plotted against potential (Fig. 7). Since the bands in Fig.
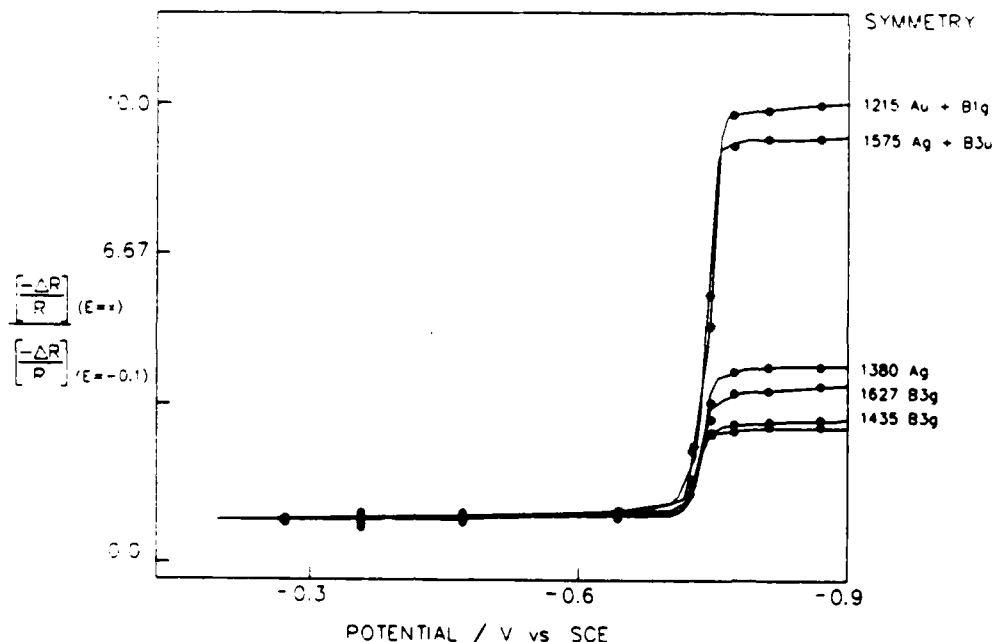
Fig. 7. Plot of the normalized intensities of the bands observed in the SNIFTIRS difference spectra at a mercury electrode in contact with a 1.3×10^{-2} mol dm^{-3} solution of isoquinoline vs. the sample potential. Reference potential = 0.0 V vs. SCE.

5 have positive values of absorbance, the positive vertical axis in Fig. 7 represents a decrease in the amount of infrared radiation absorbed. The figure shows clearly that the amount of radiation absorbed by the out-of-plane vibrational modes decreases up to a factor of 10 as the potential is changed from -0.1 to -1.0 V, wherease the in-plane vibrational modes only change by a factor of 3 to 4 over the same potential range. (We point out at this point that solution soluble isoquinoline would not exhibit this effect.)

The out-of-plane vibrational modes have dipole derivative changes perpendicular to the metal surface when the molecules are lying flat on the surface. Absorption of radiation by the surface selection rule is thus allowed. When the orientation changes to the 6,7 configuration, absorption by these modes, which are now parallel to the surface, is forbidden, as is any field induced interaction since most of the molecule lies outside of most of the field gradient. A large decrease in absorption (large increase in positive absorbance in the difference spectra) is thus expected and observed. In the case of the in-plane modes, at high electric field in the double layer leads to strong field-induced absorption for the flatly adsorbed isoquinoline, as expected. When reorienting to the 6,7 configuration, the modes become allowed by the surface selection rule. A smaller decrease in absorption is then observed.

CONCLUSIONS

The reorientations of isoquinoline molecules adsorbed onto a mercury electrode have been observed successfully by surface reflection infrared spectroscopy. It has been shown that field-induced infrared absorption makes a major contribution to the intensities of the vibrational band structure of aromatic organic molecules adsorbed on mercury.

The SNIFTIRS data show clearly that isoquinoline goes through an abrupt reorientation at potentials more negative than about -0.73 V vs. SCE (the actual transition potential being dependent on the bulk solution concentration) to the erect 6,7 standing position.

The lack of any potential dependence of the vibrational frequencies may be explained by the fact that mercury has no available vacant π-orbitals into which back-bonding (which is observed on all d metals) can occur. In this case, therefore, adsorption occurs only through σ-bonding. This point is under continued investigation.

ACKNOWLEDGEMENT

REFERENCES

1 C. Buess-Herman., N. Vanlaethem-Meuree. G. Quarin and L. Gierst. J. Electroanal. Chem., 123 (1981) 21.
2 M.W. Humphreys and R.J. Parsons. Electroanal. Chem., 82 (1977) 369.
3 R. Greef. according to ref. 2.
4 G. Quarin, C. Buess-Herman and L. Gierst. J. Electroanal. Chem., 123 (1981) 35.
5 C. Buess-Herman. J. Electroanal. Chem., 186 (1985) 27.
6 C. Buess-Herman. J. Electroanal. Chem., 186 (1985) 41.
7 C. Buess-Herman. C. Frank, C. Gierst and L. Gierst. Electrochim. Acta. 31 (1986) 965.
8 A. Bewick. private communication.
9 M.F. Crawford and R.E. MacDonald. Can. J. Phys., 36 (1958) 1022.
10 C. Korzeniewski. R.B. Shirts and S. Pons. J. Phys. Chem., 89 (1985) 2297.
11 C. Korzeniewski and S. Pons. Langmuir, 2 (1986) 468.
12 C. Korzeniewski. Ph. D Thesis. Unversity of Utah. 1987.
13 J.K. Foley. C. Korzeniewski. J.L. Daschbach and S. Pons in (Ed.). A.J. Bard, Electroanalytical Chemistry. Vol. 14. 1986. Marcel Dekker. New York. p. 309.
14 S.C. Wait. Jr. and J.C. McNerney, J. Mol. Spectrosc.. 34 (1970) 56.

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies		No. Copies
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

ABSTRACTS DISTRIBUTION LIST, SDIO/IST

Dr. Robert A. Osteryoung
Department of Chemistry
State University of New York
Buffalo, NY 14214

Dr. Douglas N. Bennion
Department of Chemical Engineering
Brigham Young University
Provo, UT 84602

Dr. Stanley Pons
Department of Chemistry
University of Utah
Salt Lake City, UT 84112

Dr. H. V. Venkatasetty
Honeywell, Inc.
10701 Lyndale Avenue South
Bloomington, MN 55420

Dr. J. Foos
EIC Labs Inc.
111 Downey St.
Norwood, MA 02062

Dr. Neill Weber
Ceramatec, Inc.
163 West 1700 South
Salt Lake City, UT 84115

Dr. Subhash C. Narang
SRI International
333 Ravenswood Ave.
Menlo Park, CA 94025

Dr. J. Paul Pemsler
Castle Technology Corporation
52 Dragon Ct.
Woburn, MA 01801

Dr. R. David Rauh
EIC Laboratory Inc.
111 Downey Street
Norwood, MA 02062

Dr. Joseph S. Foos
EIC Laboratories, Inc.
111 Downey Street
Norwood, Massachusetts 02062

Dr. Donald M. Schleich
Department of Chemistry
Polytechnic Institute of New York
333 Jay Street
Brooklyn, New York 01

Dr. Stan Szpak
Code 633
Naval Ocean Systems Center
San Diego, CA 92152-5000

Dr. George Blomgren
Battery Products Division
Union Carbide Corporation
25225 Detroit Rd.
Westlake, OH 44145

Dr. Ernest Yeager
Case Center for Electrochemical
    Science
Case Western Reserve University
Cleveland, OH 44106

Dr. Mel Miles
Code 3852
Naval Weapons Center
China Lake, CA 93555

Dr. Ashok V. Joshi
Ceramatec, Inc.
2425 South 900 West
Salt Lake City, Utah 84119

Dr. W. Anderson
Department of Electrical &
    Computer Engineering
SUNY - Buffalo
Amherst, Massachusetts 14260

Dr. M. L. Gopikanth
Chemtech Systems, Inc.
P.O. Box 1067
Burlington, MA 01803

Dr. H. F. Gibbard
Power Conversion, Inc.
495 Boulevard
Elmwood Park, New Jersey 07407

ABSTRACTS DISTRIBUTION LIST, SDIO/IST

Dr. V. R. Koch
Covalent Associates
52 Dragon Court
Woburn, MA 01801

Dr. Randall B. Olsen
Chronos Research Laboratories, Inc.
4186 Sorrento Valley Blvd.
Suite H
San Diego, CA 92121

Dr. Alan Hooper
Applied Electrochemistry Centre
Harwell Laboratory
Oxfordshire, OX11 ORA UK

Dr. John S. Wilkes
Department of the Air Force
The Frank J. Seiler Research Lab.
United States Air Force Academy
Colorado Springs, CO 80840-6528

Dr. Gary Bullard
Pinnacle Research Institute, Inc.
10432 N. Tantan Avenue
Cupertino, CA 95014

Dr. J. O'M. Bockris
Ementech, Inc.
Route 5, Box 946
College Station, TX 77840

Dr. Michael Binder
Electrochemical Research Branch
Power Sources Division
U.S. Army Laboratory Command
Fort Monmouth, New Jersey 07703-5000

Professor Martin Fleischmann
Department of Chemistry
University of Southampton
Southampton, Hants, SO9 5NH UK